

Properties changes of Ti(C, O, N) films prepared by PVD: the effect of reactive gases partial pressure

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Dark Ti-C-O-N thin films were deposited by dc reactive magnetron sputtering. A titanium target was sputtered while three different gas flows were injected into the deposition chamber: argon (working gas), acetylene and a mixture of oxygen and nitrogen (reactive gases). The films were produced with variation of the gases flow rates, maintaining the remaining parameters constant. Varying the ratio between the reactive gases flow (gas mixture/acetylene) allowed obtaining films with different characteristics. The colour of the films was characterized by spectral reflectance spectroscopy, and expressed in the CIE 1976 L*a*b* colour space. An accurate control of the deposition conditions allowed obtaining intrinsic and stable dark colours for decorative applications. Composition analysis by electron probe microanalysis was done to quantify the elemental concentrations in the films. X-ray diffraction experiments revealed the evolution of the film structure which showed to be essentially amorphous, but with evidences of fcc structure.

1. Introduction

Decorative thin films are used for a long time and their commercial importance is increasing, particularly concerning high quality products. Besides the attractive colours, the decorative coatings must supply surface quality, skin compatibility, high wear resistance and protection against corrosion. Actual technology may allow producing thin films with a wide range of colours, intrinsic or by interference. Beyond the well known golden colours achieved by TiN and ZrN, transition metal oxynitride thin films (titanium, zirconium...) are used to get brown, golden, green, purplish-pink, blue, or violet tones [1-4]. Some black coatings have been obtained, like Cu-Ni films deposited by electrochemical deposition [5], Ni-P alloys by electroless plating [6], and Ti-N-(C,Al) [7] or amorphous carbon coatings by sputtering [8], however none of these studies presents more than one black tone. As far as it is known, except a previous work of the authors of this paper, only a few publications were done on this system [9-13] and none of them focuses on the colours of these Ti-C-O-N films. The work described in this paper deals with the deposition and characterization of Ti-C-O-N decorative coatings by reactive magnetron sputtering. The goal is to economically produce coatings with several black tones. In the case of this work, only one chamber configuration was used with one target and two reactive gases: acetylene and a mixture of nitrogen and oxygen. This system allowed obtaining very dark attractive colours. The colorimetric measurements were correlated to the atomic composition and the crystallographic structure.

2. Experimental

The TiN(C,O) thin films were deposited onto single crystal silicon (100) substrates by reactive dc magnetron sputtering, consisting in two vertically opposed rectangular magnetrons (unbalanced of type 2), in a closed field configuration. The films were prepared with the substrate holder positioned at 70 mm in all runs, using a dc density of 100 A.m⁻² on the titanium target (99.6 at. %). A gas atmosphere composed of argon (working gas), nitrogen + oxygen (17:1 ratio) reactive mixture and acetylene were used for the depositions. Two different argon flows were used during the depositions: 60 and 75 sccm. The flow rate of the reactive gas mixture varied from 3 to 12.5 sccm and the acetylene flow rate varied between 7.5 and 25 sccm. The working pressure was approximately constant at 0.4 Pa and the substrates were biased ($V_B = -70$ V). During the 1 h depositions the temperature was kept constant at 473 K, using an external heating resistance. The atomic composition of the as deposited samples was measured by electron probe microanalysis (EPMA). The thickness was measured by ball cratering. The structure of the films was analyzed by X-ray diffraction (XRD) using the Cu K α radiation of a Philips PW 1710 apparatus. The characterization of film's colour was obtained with a commercial MINOLTA CM-2600d portable spectrophotometer (wavelength range: 400-700 nm), using diffused illumination at an 8° viewing angle. Colour specification was computed under the standard CIE illuminant D65 and represented in the CIELAB 1976 colour space [14,15].

3. Results and discussion

3.1 Deposition rate and composition

The gases flow rate, reactive gases flow ratio and the thickness of the produced coatings are presented in table 1.

Table 1. Gases flow rate, and reactive gases flow ratio, during depositions and thickness of Ti-C-O-N films.

Sample	$\Phi(\text{C}_2\text{H}_2)$ [sccm]	$\Phi(\text{N}_2+\text{O}_2)$ [sccm]	$\Phi(\text{Ar})$ [sccm]	$\Phi(\text{N}_2+\text{O}_2)/$ $\Phi(\text{C}_2\text{H}_2)$	Thickness [μm]
R1	15	5.5	60	0.37	1.93 ± 0.09
R2	25	4	60	0.16	1.62 ± 0.13
R3	10	8	60	0.80	1.38 ± 0.06
R4	10	4	75	0.40	1.57 ± 0.05
R5	10	10	75	1.00	1.31 ± 0.13
R6	7.5	3	75	0.40	1.23 ± 0.06
R9	7.5	5	75	0.67	1.20 ± 0.09
R10	7.5	9	75	1.20	0.90 ± 0.13
R12	7.5	12.5	60	1.6	1.09 ± 0.08

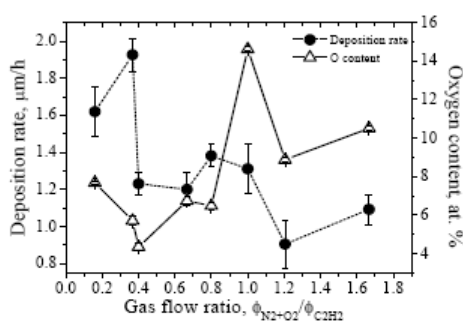


Fig. 1. Deposition rate and oxygen content of the produced Ti-C-O-N coatings as function of the gases flow ratio $\Phi(\text{N}_2+\text{O}_2)/\Phi(\text{C}_2\text{H}_2)$.

It is noticed a global decrease of the deposition rate as the reactive gases flow ratio increases. However observing with more detail it is not noticed an increase of the deposition rate for the coatings produced with lower gases flow ratios (until $(\Phi(\text{N}_2+\text{O}_2)/\Phi(\text{C}_2\text{H}_2) \approx 0.4)$ and a strong drop from ~ 2 until ~ 1.3 $\mu\text{m}/\text{h}$, which is maintained until $(\Phi(\text{N}_2+\text{O}_2)/\Phi(\text{C}_2\text{H}_2) \approx 1.0)$. Then a new drop until ~ 1 $\mu\text{m}/\text{h}$ is noticed. In terms of oxygen content in the coatings, an almost opposite behaviour may be observed. In general the oxygen content increases with the increase of the ratio $\Phi(\text{N}_2+\text{O}_2)/\Phi(\text{C}_2\text{H}_2)$. We should keep in mind that the increase of this ratio means an increase of the amount of the gas mixture inside the deposition chamber, and in consequence, an increase of the amount of oxygen (and nitrogen) in the deposition chamber. Being oxygen significantly more reactive than nitrogen or carbon, the increase of the amount of oxygen (and nitrogen) in the chamber promotes the enrichment of oxygen in the coatings, as will be analyzed, but also the target poisoning

Fig. 1 represents the deposition rate and the oxygen content of the produced TiCON films as function of the reactive gases flow ratio $(\Phi(\text{N}_2+\text{O}_2)/\Phi(\text{C}_2\text{H}_2))$.

effect and a consequent decrease of the deposition rate (Fig. 1).

Observing Fig. 2, where the variation of elemental concentration as function of the gases flow ratio two first conclusions may be pointed out: i) the global decrease of the carbon content with the increase of the gases flow ratio and ii) all the produced coatings are over-stoichiometric. Over-stoichiometry, in this case, means that the ratio between metalloid and Ti concentration is higher than unity.

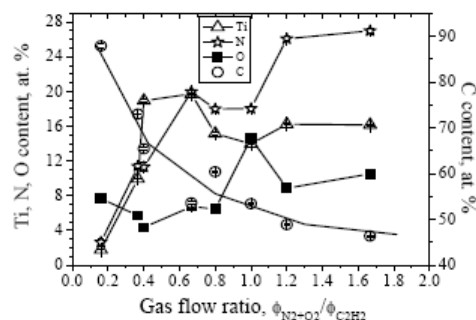


Fig. 2. Composition of the produced TiCON coatings as function of the gases flow ratio $\Phi(\text{N}_2+\text{O}_2)/\Phi(\text{C}_2\text{H}_2)$.

Moreover, relating the results of figure 1 with those of Fig. 2, it seems that the produced films may be divided in three different production zones: zone 1 ($(\Phi(\text{N}_2+\text{O}_2)/\Phi(\text{C}_2\text{H}_2) < 0.4)$ where the deposition rate increases from ~ 1.6 to ~ 2.0 $\mu\text{m}/\text{h}$, the oxygen content decreases from ~ 8 to ~ 5 at.%, nitrogen content increases from ~ 2 to ~ 12 at.%, the titanium content increases from ~ 2 to ~ 19 at.%; zone 2 ($0.4 \leq (\Phi(\text{N}_2+\text{O}_2)/\Phi(\text{C}_2\text{H}_2) \leq 1.0)$

where the deposition rate is maintained between ~ 1.2 and ~ 1.4 $\mu\text{m/h}$, the oxygen content increases from ~ 4 to ~ 14 at%, the nitrogen content is maintained around 19 at% and the titanium slightly decreases from ~ 19 to ~ 15 at%; and zone 3 ($\Phi(\text{N}_2+\text{O}_2)/\Phi(\text{C}_2\text{H}_2) > 1.0$) where the deposition rate falls to around 1 $\mu\text{m/h}$, the oxygen content falls from ~ 14 to ~ 10 at%, the nitrogen content increases to ~ 26 at% and titanium content maintains around 16 at%. This third zone corresponds to the situation where N_2 concentration in the chamber is higher than C_2H_2 concentration (Fig. 3).

The evolution of elemental composition strongly depends on the partial pressure of reactive gases in the deposition chamber. Figure 3 represents the reactive gases concentration in the deposition chamber and carbon, nitrogen and oxygen atomic content in the films. It should be noticed that the standard enthalpies of formation of TiC , TiN , TiO and TiO_2 compounds are respectively, -184 kJ/mol, -338 kJ/mol, -520 kJ/mol and -942 kJ/mol. The continuous decrease of the carbon content with the increase of the gases flow ratio may be related with the lowest value of standard enthalpy of formation for TiC .

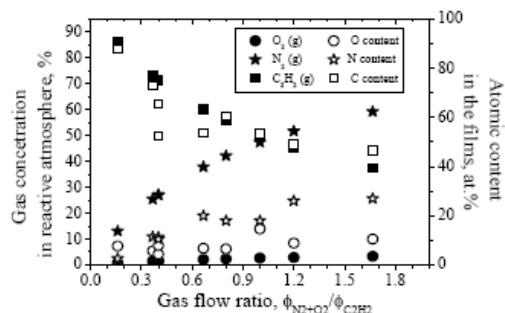


Fig. 3. Reactive gases concentration in deposition chamber (solid symbols) and composition of the produced TiCON coatings (open symbols) as function of the gas flow ratio $\Phi(\text{N}_2+\text{O}_2)/\Phi(\text{C}_2\text{H}_2)$.

The fact that the metalloid to titanium ratio is always higher than 1 makes the films with excess of $\text{N}+\text{O}+\text{C}$ in respect to titanium. It is most likely inducing some preferential reactions of Ti , according to the reactivity of each reactive gas. Anyway, despite their reactivity, the relative amount of each of the gases disposable in the deposition chamber strongly influences the resultant composition. Moreover it is important to notice that the amount of O_2 inside the chamber is always lower than 1%, and, more important, always lower than 3.5% if it is taken into account only the reactive gases, but the higher affinity of titanium towards oxygen induces much higher oxygen content in the film than the one expected from the gas mixture. Figure 3 shows that the oxygen content in the films is always higher than O_2 concentration in the chamber. This does not happen with N_2 in the case of nitrogen and with C_2H_2 in the case of carbon. Another interesting observation in figure 3 is that, despite the higher affinity of nitrogen towards titanium, when

compared with the affinity of carbon, the carbon content in the films is always higher than nitrogen content, even when the N_2 concentration in the reactive atmosphere is superior (zone 3 when $\Phi(\text{N}_2+\text{O}_2)/\Phi(\text{C}_2\text{H}_2) > 1.0$). This situation is not easy to understand but could be explained by the possibility of occurrence of other types of chemical bonds in the films. If we analyze the standard enthalpies of formation of some compounds with carbon, oxygen and nitrogen, we may have an idea of the potential bond formation in the coatings: carbon dioxide (-393.509 kJ/mol); carbon monoxide (-110.525 kJ/mol); hydrogen cyanide ($+130.5$ kJ/mol); nitrogen dioxide ($+33.1$ kJ/mol) and nitrogen monoxide ($+90.29$ kJ/mol). Taking into account these values, the C-O bonding seems to be more favorable than C-N or N-O bonding. These facts allow admitting the formation of C-O bonds competing with the formation of Ti-C and Ti-N bonding and somehow introduce, at least, part of the explanation for the relatively rich carbon content of the films when compared to nitrogen content, especially in the case of the zone 3 films. In this stage of the studies it is not possible yet to discuss the influence of the presence of hydrogen in the gas chamber. Raman spectroscopy and X-ray photoelectron spectroscopy will be used to analyze the produced films and to study the bonding states in Ti-C-O-N coatings.

3.2 Structure

The structural evolution of the $\text{Ti}(\text{C},\text{O},\text{N})$ coatings as a function of the gas flow ratio is shown in Fig. 4. X-ray diffraction patterns of the films reveal a strong dependence of the film structure on the reactive gases concentration, as well as the atomic composition. For comparison, it is shown a XRD pattern of a coating produced without gases mixture flow (equivalent to $\Phi(\text{N}_2+\text{O}_2)/\Phi(\text{C}_2\text{H}_2) = 0$). This titanium carbide film XRD pattern reveals peaks, slightly shifted to lower diffraction angles, correspond to the fcc TiC phase, appearing with a preferential orientation along the (111) direction. The (200) diffraction peak is also observed but with lower intensity. Fitting the XRD (111) and (200) peaks by a Pseudo-Voigt function the grain size in this coating was calculated and a value around 9.5 nm was obtained.

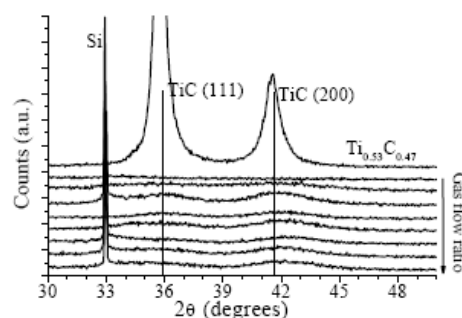


Fig. 4. XRD patterns of Ti-C-O-N coatings as function of gases flow ratio. The XRD pattern in the top corresponds to a coating deposited without nitrogen or oxygen in the chamber and is presented for comparison.

The injection of O_2+N_2 gas mixture in the deposition chamber results in coatings that clearly exhibit an amorphous structure. The long range order is lost, which may result from the joined effects of low surface diffusion of the particles impinging on the substrate, or on the growing film, and the significant over-stoichiometry of the films (Ti content is always lower than 20 at.%). Anyway the XRD pattern of some of the coatings show low intensity broad bands, around the JCPDS positions close to (111) and (200) angular positions of fcc TiC (JCPDS04-004-2919). For all the coatings produced with acetylene and the gas mixture ($N_2 + O_2$), the carbon content is always higher than nitrogen and oxygen content, and those bands may correspond to a disorganized fcc titanium carbide structure with inclusion of O and/or N atoms ($TiC_x(O,N)$). Anyway TiC, TiN and TiO present the same crystallographic structure with close lattice parameters ($a_{TiC} = 0.4328$ nm from JCPDS04-004-2919, $a_{TiN} = 0.4241$ nm, JCPDS04-001-2272 and $a_{TiO} = 0.4177$ nm, JCPDS04-001-6834). Because of this fact, XRD is not a suitable method to distinguish between these three compounds, especially in a high over-stoichiometry, like in this case. It may be possible that in the cubic lattice (significantly Ti deficient) appear many (N, O, or even C) interstitials/substitutions, which induce significant lattice distortions. Another possibility is that a nano-scaled type composite may be present, where nano-grains (cubic lattice type, with Ti vacancies and mixed O+N) are dispersed in a C amorphous matrix phase.

3.3 Colour

To obtain black coatings, and taking into account the CIE Lab colour space, the L^* colour coordinate should be low, and $|a^*|$ and $|b^*|$ should be close to zero and lower than 1.5. Actually the farther away a point from the centre $\{a^*;b^*\}=\{0;0\}$, the higher the colour saturation. Figure 5 represents the variation of the colour coordinates of the CIE Lab colour space as function of the gases flow ratio.

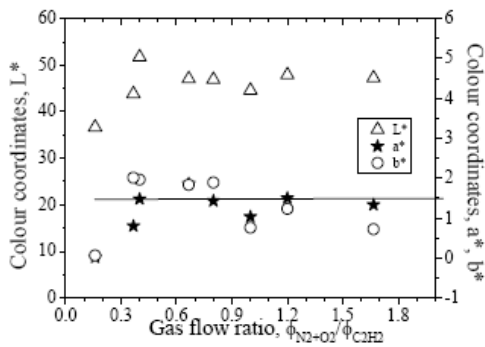


Fig. 5. Variation of the colour coordinates, $L^*a^*b^*$, of Ti-C-O-N coatings as function of gas flow ratio. The horizontal line corresponds to the positive limit of a^* and b^* coordinates for the samples to be considered black.

All the samples have a relatively low L^* value, and a^* and b^* coordinates are close to zero, and appear as black to our eyes, although with different tones, when illuminated with daylight. Once again, looking with some detail, the three zones referred above may be found. For the films of zone 1 ($\Phi(N_2+O_2)/\Phi(C_2H_2) < 0.4$) L^* increases from ~35 until ~52, a^* increases from 0 to 1.5 and b^* increases from 0 to ~2.

Above a flow ratio of 0.4, L^* maintains always between 45 and 50, but a^* and b^* maintain values between 1.5 and 2, inside zone 2 ($0.4 \leq \Phi(N_2+O_2)/\Phi(C_2H_2) \leq 1.0$), and both decrease to values between 0.5 and 1.5 inside zone 3 ($\Phi(N_2+O_2)/\Phi(C_2H_2) > 1.0$). These films of zone 3 are considered as black for a human observer and according to the industrial requirements. Curiously these coatings correspond to the samples with lower carbon content, but with higher oxygen content. Therefore the samples with the highest content of oxygen present the best colorimetric characteristics to be considered as black. This behaviour was already observed in a different set of samples produced by the authors [13].

4. Conclusions

A titanium target, argon (working gas), acetylene (carbon source) and a gas mixture (N_2+O_2) with a 17:1 ratio were used to produce reactive sputtered Ti-C-O-N coatings, varying the gases flow rate. Composition analysis reveals highly over-stoichiometric coatings which results in films with an essentially amorphous structure. For the human eye and according to industrial requirements for decorative coatings, the coatings with higher oxygen content and lower carbon content revealed to have the best colorimetric characteristics to be considered as black.

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References

- [1] N. Martin, O. Banakh, A.M.E. Santo, S. Springer, R. Sanjinés, J. Takadoum, F. Lévy, Appl. Surf. Sci. **185**, 123 (2001)
- [2] F. Vaz, P. Carvalho, L. Cunha, L. Rebouta, C. Moura, E. Alves, A. R. Ramos, A. Cavaleiro, Ph. Godeau, J. P. Rivière, Thin Solid Films **469**, 11-17 (2004).
- [3] F. Vaz, P. Cerqueira, L. Rebouta, S.M.C. Nascimento, E. Alves, Ph. Godeau, J.P. Rivière, K. Pischow, J. de Rijk, Thin Solid Films **447-448**, 449 (2004).
- [4] P. Carvalho, F. Vaz, L. Rebouta, L. Cunha, C. J. Tavares, C. Moura, E. Alves, A. Cavaleiro, Ph. Godeau, E. Le Bourhis, J. P. Rivière, J. F. Pierson, O. Banakh, Journal of Applied Physics **98**(2), 023715 (2005).

- [5] C. L. Aravinda, P. Bera, V. Jayaram, A. K. Sharma, S. M. Mayanna, *Mater. Res. Bull.* **37**, 397 (2002).
- [6] G. Cui, N. Li, D. Li, J. Zheng, Q. Wu, *Surf. Coat. Technol.* **200**, 6808 (2006).
- [7] F. Hollstein, P. Louda, *Surf. Coat. Technol.* **120–121**, 672 (1999).
- [8] M. Stüber, S. Ulrich, H. Leiste, A. Kratzsch, H. Holleck, *Surf. Coat. Technol.* **116–119**, 591 (1999).
- [9] A. Stanishevsky, R. Lappalainen, *Surf. Coat. Technol.* **123**, 101 (2000).
- [10] J. R. Sobiecki, P. Mankowski, T. Wierzchon, *Vacuum* **68**, 105 (2003).
- [11] J. H. Hsieh, W. Wu, C. Li, C. H. Yu, B. H. Tan, *Surf. Coat. Technol.* **163–164**, 233 (2003).
- [12] J. M. Chappé, A. C. Fernandes, L. Cunha, C. Moura, F. Vaz, N. Martina, D. Munteanu, B. Borcea, J. Optoelectron. *Adv. Mater.* **10**(4), 900 (2008).
- [13] J. M. Chappé, F. Vaz, L. Cunha, C. Moura, M. C. Marco de Lucas, L. Imhoff, S. Bourgeois, J. F. Pierson, *Surface & Coatings Technology* **203**, 804 (2008).
- [14] Colorimetry, CIE Publ. (Commission Internationale de L'Éclairage) 15 (1971).
- [15] Recommendations on Uniform Colour Spaces, Difference-difference equations, psychometric colour terms, CIE Publication, Suppl. N° 2-70 (Commission Internationale de L'Éclairage) 15 (1978).